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A Neutron-Diffraction Study of ZnS and ZnTe

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Accurate integrated intensities for the Bragg reflexion of neutrons by crystals of ZnS and ZnTe have been measured at room temperature. Measurements were made at a number of wavelengths and corrections were made for extinction and thermal diffuse scattering. The experimental data show contributions arising from third-order anharmonic thermal vibration of the ions. However, it is shown that, although both types of ion have a tetrahedral site symmetry and can thus give rise to such anharmonic contributions, only a single anharmonicity parameter can be determined from the neutron measurements. The magnitude of the anharmonicity parameter is similar to that obtained for the fluorine ions in CaF_2, SrF_2 and BaF_2. The nuclear scattering amplitude of zinc was refined to $b_{Zn}=0{\cdot}569(2) \times 10^{-12}$ cm, assuming a value for the nuclear scattering amplitude of sulphur of $b_S=0{\cdot}2847(1)\times 10^{-12}$ cm.

Introduction

In almost all cases determination of crystal structures is carried out using models which assume harmonic thermal vibration for all constituent atoms. The thermal vibration of each atom is thus constrained such that the time averaged probability function for the position of an atom is a Gaussian function of the displacement from its equilibrium position and contours of equal probability are ellipsoids. However, in a crystal the nearest neighbours will be arranged necessarily with a particular symmetry which one would expect to influence the thermal vibration of the atoms. For example, in a cubic crystal such as CaF_2 or ZnS, with atoms having neighbours situated at the corners of a tetrahedron, it is reasonable to expect the thermal vibration to be distorted from the harmonic cubic (spherical) symmetry by a contribution such that the atoms spend more time in directions away from the nearest neighbours than in directions towards them, *i.e.* the thermal vibration includes an anharmonic component with tetrahedral symmetry. Such anharmonic components will contribute to the diffracted Bragg intensities and can be readily observed in such structures as the fluorite structure, *e.g.* in BaF_2 contributions of about 10% have been observed in room temperature neutron-diffraction measurements. Thus careful diffraction measurements can give valuable information about the thermal vibration of the atoms and the effect on this of the site symmetry.

In earlier papers we have described series of accurate intensity measurements for the Bragg reflexion of neutrons from BaF_2 (Cooper, Rouse & Willis, 1968) and SrF_2 and CaF_2 (Cooper & Rouse, 1971). These materials all have the cubic fluorite structure and the neutron data were found to show significant effects arising from a third-order anharmonic component in the thermal vibration of the fluorine ions, as allowed by their non-centrosymmetric site symmetry. These earlier measurements thus confirmed the importance of anharmonic effects for atoms occupying tetrahedral sites in the fluorite structure and further measurements have now been carried out in order to explore the possible importance of anharmonic effects in other types of structure. The present paper describes measurements which have been made on crystals of ZnS and ZnTe.

Considerable care was exercised in these measurements in order to achieve data which were considered to be reliable to the required level of accuracy. The appropriate experimental techniques and the sources of systematic error which need to be considered in this type of work have been discussed elsewhere (Cooper & Rouse, 1970*a*). Measurements were made at several wavelengths in order to determine wavelength independent parameters more precisely and to provide a check on the validity of the interpretation of wavelength dependent effects.

ZnS and ZnTe can both occur with either a cubic, zinc blende structure or a hexagonal, wurtzite structure. In both types of structure each ion is surrounded by four ions of the opposite type situated at the corners of a regular tetrahedron and the structures differ essentially only in whether the coordination tetrahedra are packed with a cubic or hexagonal symmetry. Polytypic growth can also occur, in which periodic repetition of stacking faults leads to a series of possible hexagonal structures which are identical in the **a** and **b** directions and differ only in the **c** direction (see for example, Rai, 1971). Rai (1971) points out that the polytypic growth in ZnS is a result of the ordering of face-centred cubic microtwins along the [111] directions. A polytype can thus be considered in terms of stacking faults arising in the packing of the coordination tetrahedra such that the resultant hexagonal structures can be considered in terms of cubic microtwins. The local environment of a single ion is the same in all these structures, *i.e.* a tetrahedron, and for simplicity we shall consider the theory in detail only for the cubic, zinc blende structure.

Theory

A general structure-factor formalism for interpreting accurate X-ray and neutron-diffraction data has been outlined by Dawson (1967) and we shall base our own formalism on that of Dawson, applying it particularly to the case of the zinc blende structure. We shall consider specifically the case of neutron diffraction and we shall therefore use the scattering vector **Q**, related to the S used by Dawson by $\mathbf{Q}=2\pi\mathbf{S}$.

Dawson shows that the structure factor $F(\mathbf{Q})$ for a particular scattering vector **Q** can be written in terms of the scattering factors $f_j(\mathbf{Q})$ and the thermal vibration factors $T_j(\mathbf{Q})$ of the atoms positions $\mathbf{r}_j$ in the unit cell:

$$F(\mathbf{Q})=\sum_j f_j(\mathbf{Q})T_j(\mathbf{Q})\exp(i\mathbf{Q}\,.\,\mathbf{r}_j)\,. \tag{1}$$

In general the atomic functions may contain non-centrosymmetric components and both $f_j(\mathbf{Q})$ and $T_j(\mathbf{Q})$ may be complex, so that we should write:

$$f_j(\mathbf{Q})=f_{cj}(\mathbf{Q})+if_{aj}(\mathbf{Q}) \tag{2}$$

$$T_j(\mathbf{Q})=T_{cj}(\mathbf{Q})+iT_{aj}(\mathbf{Q}) \tag{3}$$

where the suffices c and a refer to the centrosymmetric and anticentrosymmetric components respectively.

Since we are considering specifically the case for neutron diffraction we can replace the complex $f_j(\mathbf{Q})$ by the real nuclear scattering amplitude b_j.

Equation (1) can then be written in the form:

$$F(\mathbf{Q})=\sum_j b_j[T_{cj}(\mathbf{Q})+iT_{aj}(\mathbf{Q})]\exp(i\mathbf{Q}\,.\,\mathbf{r}_j) \tag{4}$$

$$\begin{aligned}=\sum_j b_j\{&[T_{cj}(\mathbf{Q})\cos\mathbf{Q}\,.\,\mathbf{r}_j-T_{aj}(\mathbf{Q})\sin\mathbf{Q}\,.\,\mathbf{r}_j]\\&+i[T_{cj}(\mathbf{Q})\sin\mathbf{Q}\,.\,\mathbf{r}_j+T_{aj}(\mathbf{Q})\cos\mathbf{Q}\,.\,\mathbf{r}_j]\}\,.\end{aligned} \tag{5}$$

For the zinc blende (ZnS) structure the structure factors take one of three forms, depending on the index sum $h+k+l$ being equal to $4n$, $4n+2$, or $4n\pm1$, where n is an integer. Considering the zinc atoms to be at 0,0,0 and equivalent sites and the sulphur atoms to be at $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ and equivalent sites, we therefore have the following relationships for the various groups of reflexions.

(*a*) $h+k+l=4n$

$\cos\mathbf{Q}\,.\,\mathbf{R}_j=1$ and $\sin\mathbf{Q}\,.\,\mathbf{r}_j=0$ for all atoms and

$$\begin{aligned}F(\mathbf{Q})=&\,4b_{\mathrm{Zn}}T_{c\mathrm{Zn}}(\mathbf{Q})+4b_{\mathrm{S}}T_{c\mathrm{S}}(\mathbf{Q})\\&+i[4b_{\mathrm{Zn}}T_{a\mathrm{Zn}}(\mathbf{Q})+4b_{\mathrm{S}}T_{a\mathrm{S}}(\mathbf{Q})]\,.\end{aligned} \tag{6}$$

(*b*) $h+k+l=4n+2$

$$\cos\mathbf{Q}\,.\,\mathbf{r}_{\mathrm{Zn}}=1,\ \ \sin\mathbf{Q}\,.\,\mathbf{r}_{\mathrm{Zn}}=0\,,$$
$$\cos\mathbf{Q}\,.\,\mathbf{r}_{\mathrm{S}}=-1,\ \ \sin\mathbf{Q}\,.\,\mathbf{r}_{\mathrm{S}}=0$$

and

$$\begin{aligned}F(\mathbf{Q})=&\,4b_{\mathrm{Zn}}T_{c\mathrm{Zn}}(\mathbf{Q})-4b_{\mathrm{S}}T_{c\mathrm{S}}(\mathbf{Q})\\&+i[4b_{\mathrm{Zn}}T_{a\mathrm{Zn}}(\mathbf{Q})-4b_{\mathrm{S}}T_{a\mathrm{S}}(\mathbf{Q})]\,.\end{aligned} \tag{7}$$

(*c*) $h+k+l=4n\pm1$

$$\cos\mathbf{Q}\,.\,\mathbf{r}_{\mathrm{Zn}}=1,\ \ \sin\mathbf{Q}\,.\,\mathbf{r}_{\mathrm{Zn}}=0\,,$$
$$\cos\mathbf{Q}\,.\,\mathbf{r}_{\mathrm{S}}=0,\ \ \sin\mathbf{Q}\,.\,\mathbf{r}_{\mathrm{S}}=\pm1$$

and

$$\begin{aligned}F(\mathbf{Q})=&\,4b_{\mathrm{Zn}}[T_c(\mathbf{Q})+iT_a(\mathbf{Q})]_{\mathrm{Zn}}\\&\pm i4b_{\mathrm{S}}[T_c(\mathbf{Q})+iT_a(\mathbf{Q})]_{\mathrm{S}}\end{aligned} \tag{8}$$

$$\begin{aligned}=4\{&[b_{\mathrm{Zn}}T_{c\mathrm{Zn}}(\mathbf{Q})\mp b_{\mathrm{S}}T_{a\mathrm{S}}(\mathbf{Q})]\\&+i[b_{\mathrm{Zn}}T_{a\mathrm{Zn}}(\mathbf{Q})\pm b_{\mathrm{S}}T_{c\mathrm{S}}(\mathbf{Q})]\}\,.\end{aligned} \tag{9}$$

Hence, if $T_{aj}\ll T_{cj}$ and the real terms are not extremely small, we can ignore the imaginary terms in equations (6) and (7) and equation (9) gives, for $h+k+l=4n\pm1$,

$$\begin{aligned}F(\mathbf{Q})F^*(\mathbf{Q})=16\{&[b^2_{\mathrm{Zn}}T^2_{c\mathrm{Zn}}(\mathbf{Q})+b^2_{\mathrm{S}}T^2_{c\mathrm{S}}(\mathbf{Q})]\\&\mp2b_{\mathrm{Zn}}b_{\mathrm{S}}[T_{c\mathrm{Zn}}(\mathbf{Q})T_{a\mathrm{S}}(\mathbf{Q})-T_{a\mathrm{Zn}}(\mathbf{Q})T_{c\mathrm{S}}(\mathbf{Q})]\}\,.\end{aligned} \tag{10}$$

Thus the contribution to the neutron Bragg intensity arising from anharmonic thermal vibrations is significant only for reflexions with $h+k+l=4n\pm1$ and is given by

$$\begin{aligned}(\Delta I)_a=\mp32b_{\mathrm{Zn}}b_{\mathrm{S}}[&T_{c\mathrm{Zn}}(\mathbf{Q})T_{a\mathrm{S}}(\mathbf{Q})\\&-T_{a\mathrm{Zn}}(\mathbf{Q})T_{c\mathrm{S}}(\mathbf{Q})]\,.\end{aligned} \tag{11}$$

Ignoring fourth and higher-order terms, the one particle potential appropriate to a tetrahedral site symmetry is

$$V_j(\mathbf{u})=V_{oj}+\tfrac{1}{2}\alpha_j(x^2+y^2+z^2)+\beta_j(xyz) \tag{12}$$

where x, y and z are the coordinates defining the instantaneous displacement **u** of the jth atom and the parameter α_j is related to the mean-square displacement of the atom in this potential, including the effect of thermal expansion.

The one-particle potential defined in equation (12) gives the following expressions for the thermal vibration factors:

$$T_{cj}(\mathbf{Q})=\exp\left(-\frac{Q^2k_BT}{2\alpha_j}\right) \qquad (13)$$

$$T_{aj}(\mathbf{Q})=\beta_j\,\frac{(k_BT)^2}{\alpha_j^3}\left(\frac{2\pi}{a_0}\right)^3 T_{cj}(\mathbf{Q})hkl \qquad (14)$$

where a_0 is the unit cell side.

The conventional harmonic temperature factor is given by

$$B_j=8\pi^2k_BT/\alpha_j\,. \qquad (15)$$

For ZnS β_j is finite for both ions but $\beta_{\rm Zn}$ and $\beta_{\rm S}$ will have opposite signs so that the anharmonic effects arising from the two ions will be additive. The resultant contribution to the neutron Bragg intensity for reflexions with $h+k+l=4n\pm1$ is obtained by substituting equations (13) and (14) into equation (11), and is

$$(\Delta I)_a=\mp 32b_{\rm Zn}b_{\rm S}\exp\left(-\frac{Q^2k_BT}{2\alpha_{\rm Zn}}\right)\exp\left(-\frac{Q^2k_BT}{2\alpha_{\rm S}}\right)$$
$$\times(k_BT)^2\left(\frac{2\pi}{a_0}\right)^3 hkl\left(\frac{\beta_{\rm S}}{\alpha_{\rm S}^3}-\frac{\beta_{\rm Zn}}{\alpha_{\rm Zn}^3}\right)\,. \qquad (16)$$

This contribution is proportional to the product $h\times k\times l$, as in the case of the fluorite structure, but in the case of ZnS depends on a weighted difference of $\beta_{\rm S}$ and $\beta_{\rm Zn}$, where the weights are $1/\alpha_{\rm S}^3$ and $1/\alpha_{\rm Zn}^3$ respectively. It is possible to determine only one parameter to describe the anharmonic behaviour and for convenience we shall therefore consider an effective anharmonic thermal parameter $\beta'=\beta_{\rm S}-(\alpha_{\rm S}^3/\alpha_{\rm Zn}^3)\beta_{\rm Zn}$.

Experimental measurements

The samples used were spherical crystals of ZnS and ZnTe, of radii 1·1 mm and 1·0 mm respectively, which were cut from crystals supplied by Semi-Elements Inc. as single crystals of cubic material[†]. In both cases a crystallographic [110] axis was aligned vertically and two-dimensional *hkk* intensity measurements were made using a Hilger and Watts Mk. II automatic neutron diffractometer.

Initial intensity measurements from both crystals were found to be inconsistent with them being cubic single crystals, the intensities of certain reflexions being enhanced by approximately 40%. These reflexions were found to belong to certain groups depending systematically on their indices, and the observations were interpreted successfully in terms of a twinning about a cubic [111] axis, resulting in coincidence between certain reflexions from each twin. Further measurements of reflexions from both twins confirmed these conclusions and no evidence could be found of twinning about any other axis. It was thus shown that in both cases the crystals could be considered, as far as the fundamental Bragg reflexions are concerned, as two cubic macro-twins with the intensity from one twin being about 2½ times the intensity from the other. However, other crystals of ZnS cut from the same source crystal showed identical properties and it seems probable, therefore, that the crystals were in fact polytypes consisting of series of cubic micro-twins. However, the purpose of the present study was to investigate the diffraction of neutrons by a region of material with cubic structure and no further study of polytypic properties was undertaken.

In order to avoid complications arising from the twinning, subsequent measurements were restricted to reflexions which arose only from scattering from the larger twin. In all cases intensities were averaged over an appropriate two-dimensional set of equivalent reflexions (hkk and $\bar{h}\bar{k}\bar{k}$, $\bar{h}kk$ and $h\bar{k}\bar{k}$ or hkk, $\bar{h}\bar{k}\bar{k}$, $\bar{h}kk$ and $h\bar{k}\bar{k}$). Reflexions were scanned in a θ–2θ mode using a rectangular detector aperture which was adjusted to reduce the amount of background scattering detected, without any loss of Bragg intensity. A minimum scan range of ± 1·0° was used throughout, but for the highest angle reflexions the scan range was increased in order to avoid possible loss of Bragg intensity. No anomalies were observed in the background scattering and background measurements were therefore made using a similar scan with the crystal mis-set by 2°. Measurements were made at three different wavelengths for ZnS in order to determine the wavelength independent parameters more precisely and to check on the consistency of wavelength dependent effects. In the case of ZnTe, however, measurements were made at two wavelengths only because of limitations arising in the analysis of the data due to the similarity of the neutron-scattering amplitudes of zinc and tellurium.

Data analysis

(*a*) *Method of analysis*

The sets of observed data were analysed using the Harwell *TAILS* computer program, which was developed originally for the analysis of data involving effects due to anharmonic thermal vibrations and requiring possible corrections for extinction and thermal diffuse scattering. The program determines the values of the varied parameters which minimize the quantity S, given by

$$S=\sum_i\,[w_i(I_{oi}-I_{ci})]^2 \qquad (17)$$

[†] Chemical analyses indicated that the samples were of equiatomic composition within experimental error and that there were negligible amounts of metallic impurities. Lattice constants were determined by X-ray photographic methods to be $a=5{\cdot}410$ (1) Å for ZnS and $a=6.100$ (2) Å for ZnTe; both these values are in good agreement with previously published values and are consistent with equiatomic stoichiometric composition.

where I_{oi} is the observed background corrected intensity of the ith reflexion, I_{ci} is the corresponding computed quantity and w_i is the weight given to the observation.

It should be noted that for spherical or cylindrical crystals no corrections, apart from the subtraction of the normal background, are made to the observed intensities; corrections for all systematic effects are made to the computed intensities. Minimization of S is effected by the search algorithm of Powell (1965), implemented in the subroutine *VA*02*A* of the Harwell subroutine library. This algorithm does not necessitate the computation of partial derivatives.

Provision is made for including corrections for the effects of absorption, extinction and thermal diffuse scattering, the calculated intensity being given by

$$I_c = sA_\mu(y+\alpha)|F_c|^2 \operatorname{cosec} 2\theta \qquad (18)$$

where s is the scale factor, A_μ the absorption factor, y the extinction factor and α the thermal diffuse scattering factor.

The absorption factor for a spherical or cylindrical crystal is obtained by interpolation in stored tables of A_μ as a function of μR and $\sin^2\theta$, where R is the radius of the crystal. Tables appropriate to neutron-diffraction measurements have been published elsewhere (Rouse, Cooper, York & Chakera, 1970). For other shapes of crystals it is necessary to correct the observed intensities for absorption.

The extinction factor is that defined by the Zachariasen (1967) theory as modified by the authors [Cooper & Rouse, 1970*b*, equations (29), (34), (15) and (20*d*)].

The thermal diffuse scattering factor is calculated using the isotropic approximation of the authors (Cooper & Rouse, 1968) for first-order scattering, but it should be noted that this approximation is not valid if the neutron velocity is appreciably less than that of the phonons concerned (see Cooper, 1971).

(*b*) *Results*

Absorption was sufficiently small in the crystals studied ($\mu R < 0.01$) for A_μ to be considered the same for all reflexions and this factor was therefore considered as part of the scaling factor. Thermal diffuse scattering corrections were calculated using the elastic constant values tabulated by Fedorov(1968) for ZnS. No values were available for ZnTe and the ZnS values were therefore used as a first approximation. Analyses using other values confirmed that the only parameters which will be in error if the elastic constant values are not appropriate are the harmonic thermal parameters (α_{Zn} and α_{Te}).

The parameters which were considered as possible variable quantities were the scale factors, the nuclear scattering amplitude of zinc, the harmonic thermal parameters for each ion, the effective anharmonic thermal parameter and the effective domain radius r^*. The nuclear scattering amplitudes of sulphur and tellurium were taken to be $b_S = 0.2847 \times 10^{-12}$ cm and $b_{Te} = 0.543 \times 10^{-12}$ cm (Koester, 1971), but it should be noted that, since the scale factor is refined, only the ratio of the scattering amplitudes of the cation and anion can be determined from the analysis.

Table 1. *Neutron diffraction data for* ZnS *at* $\lambda = 0.873$ Å

h k l	I_o	I_c	$\sigma(I_o)$	y	α
0 2 2	45672	45445	154	0.878	0.002
4 0 0	30534	30933	188	0.916	0.006
4 2 2	24142	23845	232	0.936	0.010
0 4 4	19066	19391	144	0.948	0.015
4 4 4	13800	13914	176	0.963	0.026
8 0 0	10584	10656	112	0.972	0.037
8 2 2	9192	9490	150	0.975	0.043
4 6 6	7690	7777	117	0.980	0.056
8 4 4	7105	7153	88	0.982	0.062
2 0 0	8053	8142	67	0.978	0.001
2 2 2	4527	4252	63	0.988	0.004
2 4 4	1816	1792	43	0.995	0.018
6 2 2	1519	1463	30	0.996	0.023
6 4 4	808	878	28	0.998	0.040
2 6 6	800	759	27	0.998	0.047
10 0 0	607	521	38	0.999	0.065
10 2 2	607	471	38	0.999	0.071
1 1 1	(41596)	43211	202	0.883	0.001
3 1 1	22432	22450	107	0.940	0.004
1 3 3	15664	15854	89	0.957	0.008
5 1 1	12408	12400	100	0.967	0.012
5 3 3	8556	8486	60	0.977	0.022
7 1 1	7339	7312	79	0.980	0.028
1 5 5	7192	7287	79	0.981	0.028
3 5 5	6305	6406	56	0.983	0.034
7 3 3	5598	5635	50	0.985	0.039
5 5 5	5077	4919	65	0.987	0.045
9 1 1	4498	4483	46	0.988	0.051
1 7 7	3778	3746	55	0.990	0.064
7 5 5	3742	3838	55	0.990	0.064
3 7 7	3560	3574	35	0.991	0.070
11 1 1	3460	3255	53	0.992	0.080
5 7 7	3182	3164	48	0.992	0.080

Table 2. *Neutron diffraction data for* ZnS *at* $\lambda = 0.945$ Å

h k l	I_o	I_c	$\sigma(I_o)$	y	α
0 2 2	79893	79823	202	0.846	0.003
4 0 0	56180	55273	169	0.893	0.007
4 2 2	42989	43148	211	0.917	0.013
0 4 4	34870	35475	135	0.932	0.018
4 4 4	25821	26066	165	0.950	0.031
8 0 0	20604	20542	105	0.962	0.044
8 2 2	18838	18624	142	0.965	0.050
4 6 6	16148	16065	94	0.970	0.065
8 4 4	15539	15342	131	0.972	0.071
2 0 0	14715	14689	90	0.971	0.001
2 2 2	7808	7741	69	0.985	0.005
2 4 4	3193	3343	30	0.994	0.021
6 2 2	2633	2757	26	0.995	0.028
6 4 4	1710	1724	16	0.997	0.047
2 6 6	1455	1517	13	0.997	0.054
10 0 0	1144	1155	11	0.998	0.074
10 2 2	1093	1116	10	0.998	0.078
1 1 1	76674	76432	280	0.853	0.001
3 1 1	40246	39870	145	0.922	0.004
1 3 3	28688	28744	122	0.944	0.009
5 1 1	22763	22712	155	0.956	0.015
5 3 3	16063	15869	93	0.970	0.027
7 1 1	13909	13835	123	0.974	0.033
1 5 5	13864	13790	123	0.974	0.033
3 5 5	12265	12285	82	0.977	0.040
7 3 3	10897	10980	78	0.979	0.046
5 5 5	9756	9770	75	0.982	0.053
9 1 1	8926	9139	72	0.983	0.061
1 7 7	8150	8212	44	0.985	0.073
7 5 5	8490	8412	44	0.985	0.073
3 7 7	8388	8338	71	0.985	0.078

Of the remaining parameters only the scale factor and the effective domain radius vary with the wavelength. However, the original version of the program does not permit joint refinement of data collected at different wavelengths and initial analysis was carried out treating the data for the various wavelengths separately. Good agreement was obtained for the values of parameters which are independent of wavelength and a weighted mean value was determined in each case. The analysis was then repeated with these parameters fixed at their weighted mean values, in the following order: (i) zinc scattering amplitude, (ii) harmonic thermal parameters, (iii) effective anharmonic thermal parameters. Because of correlation problems arising from the similarity between the values of the nuclear scattering amplitudes of zinc and tellurium no attempt was made to refine the value of b_{Zn} from the ZnTe data. Instead, its value was fixed at that obtained from the analysis of the ZnS data. Because of this similarity the intensities of the reflexions with $h+k+l=4n+2$ were very small and they were not measured at the lower wavelength.

Table 3. *Neutron diffraction data for* ZnS *at* $\lambda=1{\cdot}146$ Å

h k l	I_o	I_c	$\sigma(I_o)$	y	α
0 2 2	(47645)	50946	220	0.807	0.003
4 0 0	(37782)	36376	196	0.862	0.007
4 2 2	29055	29161	121	0.890	0.011
0 4 4	24673	24687	159	0.907	0.017
4 4 4	19276	19586	70	0.927	0.028
8 0 0	17935	17680	68	0.935	0.039
8 2 2	18008	18102	96	0.934	0.043
2 0 0	10043	9668	36	0.962	0.001
2 2 2	5197	5201	22	0.980	0.005
2 4 4	2345	2421	12	0.991	0.020
6 2 2	2038	2072	13	0.992	0.025
6 4 4	1636	1606	10	0.994	0.041
2 6 6	1676	1670	8	0.994	0.044
1 1 1	(50454)	48462	226	0.816	0.001
3 1 1	26509	26195	116	0.899	0.004
1 3 3	19216	19367	71	0.926	0.009
5 1 1	15571	15694	63	0.940	0.014
5 3 3	11615	11724	45	0.955	0.024
7 1 1	10768	10719	57	0.959	0.031
1 5 5	10817	10684	53	0.959	0.031
3 5 5	10021	10142	56	0.962	0.036
7 3 3	9982	9944	56	0.963	0.041
5 5 5	10237	10296	42	0.962	0.044

Table 4. *Neutron diffraction data for* ZnTe *at* $\lambda=0{\cdot}945$ Å

h k l	I_o	I_c	$\sigma(I_o)$	y	α
0 2 2	31428	31837	178	0.889	0.002
4 0 0	21628	21561	150	0.924	0.004
4 2 2	16314	16568	136	0.942	0.007
0 4 4	13798	13437	118	0.953	0.011
4 4 4	9900	9599	89	0.967	0.018
8 0 0	7461	7316	82	0.975	0.027
8 2 2	6500	6496	82	0.978	0.031
4 6 6	5172	5276	60	0.982	0.040
8 4 4	4723	4820	83	0.984	0.045
4 8 8	3677	3822	76	0.987	0.066
1 1 1	28618	27826	177	0.902	0.000
3 1 1	14228	14071	90	0.950	0.003
1 3 3	9938	10010	76	0.964	0.005
5 1 1	7830	7829	98	0.972	0.009
5 3 3	5380	5377	59	0.981	0.016
7 1 1	4413	4639	78	0.984	0.020
1 5 5	4562	4625	79	0.984	0.020
3 5 5	3982	4069	53	0.986	0.024
7 3 3	3648	3589	54	0.988	0.028
5 5 5	3010	3151	74	0.989	0.032
9 1 1	2900	2870	45	0.990	0.037
1 7 7	2353	2399	55	0.992	0.046
7 5 5	2300	2447	63	0.992	0.046
3 7 7	2178	2270	54	0.992	0.051
11 1 1	1821	2022	64	0.993	0.059
5 7 7	2044	1979	72	0.993	0.059
9 5 5	1788	1934	48	0.994	0.062
11 3 3	1830	1994	49	0.993	0.065

Table 5. *Neutron diffraction data for* ZnTe *at* $\lambda=1{\cdot}143$ Å

h k l	I_o	I_c	$\sigma(I_o)$	y	α
0 2 2	17566	18391	137	0.924	0.002
4 0 0	12137	12462	114	0.948	0.004
4 2 2	9197	9658	71	0.960	0.007
0 4 4	7389	7934	64	0.967	0.010
4 4 4	5852	5898	69	0.976	0.017
8 0 0	4508	4784	40	0.980	0.024
8 2 2	4608	4447	37	0.982	0.028
4 6 6	4311	4173	36	0.983	0.035
8 4 4	4463	4341	37	0.983	0.037
2 0 0	42	8	32	1.000	0.001
2 2 2	26	0	31	1.000	0.003
2 4 4	0	13	28	1.000	0.012
6 2 2	17	20	20	1.000	0.015
6 4 4	37	47	16	1.000	0.026
2 6 6	66	57	16	1.000	0.030
10 0 0	54	115	23	1.000	0.038
1 1 1	16192	15887	76	0.934	0.000
3 1 1	8032	7994	48	0.966	0.002
1 3 3	5788	5737	40	0.976	0.005
5 1 1	4427	4546	36	0.981	0.008
5 3 3	3231	3239	32	0.987	0.015
7 1 1	2828	2866	21	0.988	0.018
1 5 5	2784	2858	21	0.988	0.018
3 5 5	2553	2593	24	0.989	0.022
7 3 3	2462	2380	21	0.990	0.026
5 5 5	2273	2198	20	0.991	0.029
9 1 1	2201	2145	20	0.991	0.033
1 7 7	2417	2320	17	0.991	0.037
7 5 5	2469	2365	17	0.991	0.037

The final values of the effective domain radii (r^*) were found, in both cases, to be consistent with the wavelength dependence predicted by the Zachariasen theory [see Cooper & Rouse, 1970*b*, equation (16*d*)]. Final analyses of the data were therefore carried out with domain radius (r) and mosaic spread (g) parameters fixed at values determined from the individual r^* values. The final models are therefore identical for all wavelengths.

Discussion

The experimental data are summarized in Tables 1 to 3 for ZnS and Tables 4 and 5 for ZnTe. These tables list the observed and calculated background-corrected intensities, the standard deviations of the observed intensities based on counting statistics, together with the values of the extinction and thermal diffuse scattering factors for each reflexion. The observed intensities given in brackets for ZnS were omitted from the analysis to avoid any distortion of the model by forcing it to give a better agreement for the strongest reflexions, particularly for the longest wavelength when factors such as anisotropy in the extinction may become important for these.

In order to give an indication of the overall agreement, the values of the discrepancy index

$$R_I = \sum_i |I_{oi} - I_{ci}| / \sum_i I_{oi} \tag{19}$$

are listed for the various sets of data in Table 6. The final values of the varied parameters are listed in Table 7 and the derived values of the structure factors are given in Table 8 for ZnS and Table 9 for ZnTe.

Table 6. *Discrepancy index values* (%)

λ(Å)	ZnS	λ(Å)	ZnTe
0·873	1·30	0·945	1·96
0·945	0·74	1·143	3·24
1·146	0·94		

Table 7. *Final values of parameters for* ZnS *and* ZnTe

	ZnS	ZnTe	
b_{Zn}	0·569 (0·002)	–	$\times 10^{-12}$ cm
α_{Zn}	3·633 (0·019)	2·463 (0·065)	$\times 10^{-12}$ erg.Å^{-2}
$\alpha_{\mathrm{S(Te)}}$	4·408 (0·024)	4·213 (0·062)	$\times 10^{-12}$ erg.Å^{-2}
$-\beta'$	4·2 (1·1)	3·8 (1·0)	$\times 10^{-12}$ erg.Å^{-3}
B_{Zn}	0·879 (0·005)	1·296 (0·034)	Å^2
$B_{\mathrm{S(Te)}}$	0·724 (0·004)	0·758 (0·011)	Å^2
r	$\gg 1$	4·14 *	$\times 10^{-5}$ cm
g	1390 (360)	1300 *	

* Fitted to two r^* values only; uncertainties will be very large (see text).

Table 8. *Neutron structure factors for* ZnS

	0.873Å	0.945Å	1.146Å	
h k l	F_1	F_2	F_3	F_c
0 2 2	3.234	3.227	(3.120)	3.226
4 0 0	3.029	3.074	(3.107)	3.049
4 2 2	2.899	2.876	2.876	2.881
0 4 4	2.700	2.700	2.722	2.723
4 4 4	2.423	2.421	2.413	2.432
8 0 0	2.166	2.176	2.189	2.173
8 2 2	2.022	2.066	2.049	2.054
4 6 6	1.825	1.840		1.835
8 4 4	1.729	1.746		1.735
2 0 0	1.091	1.098	1.118	1.096
2 2 2	1.054	1.026	1.021	1.022
2 4 4	0.830	0.806	0.812	0.825
6 2 2	0.782	0.750	0.761	0.767
6 4 4	0.592	0.615	0.623	0.618
2 6 6	0.589	0.562	0.575	0.574
10 0 0	0.497	0.458		0.460
10 2 2	0.485	0.423		0.427
1 1 1	(2.441)	2.493	(2.540)	2.489
3 1 1	2.359	2.361	2.364	2.350
1 3 3	2.203	2.214	2.207	2.216
5 1 1	2.092	2.094	2.084	2.092
5 3 3	1.867	1.871	1.851	1.860
7 1 1	1.763	1.765	1.764	1.760
1 5 5	1.746	1.762	1.768	1.757
3 5 5	1.654	1.666	1.657	1.667
7 3 3	1.568	1.567	1.576	1.573
5 5 5	1.493	1.469	1.466	1.470
9 1 1	1.399	1.380		1.396
1 7 7	1.247	1.237		1.242
7 5 5	1.241	1.263		1.257
3 7 7	1.183	1.189		1.185
11 1 1	1.081			1.049
5 7 7	1.037			1.034

Table 9. *Neutron structure factors for* ZnTe

	0.945Å	1.143Å	
h k l	F_1	F_2	F_c
0 2 2	4.180	4.112	4.207
4 0 0	3.987	3.928	3.980
4 2 2	3.738	3.676	3.767
0 4 4	3.613	3.440	3.565
4 4 4	3.246	3.183	3.196
8 0 0	2.895	2.783	2.867
8 2 2	2.717	2.765	2.716
4 6 6	2.416	2.480	2.440
8 4 4	2.290	2.346	2.314
4 8 8	1.655		1.687
2 0 0		0.164	0.070
2 2 2		0.167	0.007
2 4 4		0.000	0.146
6 2 2		0.168	0.185
6 4 4		0.248	0.279
2 6 6		0.324	0.302
10 0 0		0.242	0.353
1 1 1	3.124	3.110	3.080
3 1 1	2.930	2.921	2.914
1 3 3	2.746	2.768	2.756
5 1 1	2.609	2.575	2.609
5 3 3	2.338	2.334	2.337
7 1 1	2.165	2.205	2.220
1 5 5	2.202	2.189	2.217
3 5 5	2.089	2.095	2.112
7 3 3	2.018	2.036	2.002
5 5 5	1.841	1.916	1.884
9 1 1	1.807	1.821	1.798
1 7 7	1.604	1.653	1.619
7 5 5	1.585	1.671	1.635
3 7 7	1.520		1.552
11 1 1	1.324		1.396
5 7 7	1.403		1.380
9 5 5	1.264		1.315
11 3 3	1.215		1.268

It can be seen from Tables 8 and 9 that there is eccellent agreement between the observed structure factors derived from the various sets of data. Extinction effects were relatively small in both crystals with very few reflexions being reduced in intensity by more than 10% because of extinction. The measurements as a whole agree well with the Zachariasen (1967) theory of extinction as extended by the authors (Cooper & Rouse, 1970*b*). The observed values of the effective domain radius r^* are listed in Table 10. The effective domain radius is related to the true domain radius r and the mosaic spread parameter g by equation (16*d*) of Cooper & Rouse (1970*b*), *viz*:

$$r^* = r/[1 + (r/\lambda g)^2]^{1/2}. \tag{20}$$

Table 10. *Effective domain radius values* ($\times 10^{-5}$ cm) *for* ZnS *and* ZnTe

	λ(Å)	r^*	$\sigma(r^*)$	r^*_{calc}
ZnS	0·873	1·19	0·04	1·21
	0·945	1·34	0·07	1·47
	1·146	1·67	0·18	1·59
ZnTe	0·945	1·18	0·14	1·18
	1·143	1·40	0·68	1·40

The values of r and g which give r^* values in the best agreement with the individually refined values given in Table 10 are $r \gg 10^{-5}$ cm and $g = 1390$ for ZnS and $r = 4{\cdot}14 \times 10^{-5}$ cm and $g = 1300$ for ZnTe. The r^* values given by these r and g values are also listed in Table 10. It should be emphasized, however, that the interpretation of the extinction parameters in terms of r and g values must be treated with extreme caution since the standard deviations of the individual refined r^* values are such that the uncertainty in the values of r and g will be extremely large. This is particularly true for ZnTe for which we have only two r^* values. Thus, although it is possible to use a single model for the extinction properties to account for the observations at all wavelengths, the extinction properties are described more satisfactorily in terms of the effective domain radius values.

On the basis of the extinction parameters it would appear that the ZnS crystal is a type I crystal in which $r \gg \lambda g$ and the extinction depends essentially on g only. Although the r^* values for ZnTe indicate a tendency towards type I with $r > \lambda g$ the uncertainties involved are such that no reliable conclusions can be drawn. Thus, one factor which emerges clearly from this analysis is the danger associated with the derivation of r and g values from data obtained at two wavelengths only.

There appear to be no previously published measurements on ZnS or ZnTe with which we may compare the values obtained for the harmonic thermal vibration parameters. However, recent unpublished X-ray diffraction measurements on ZnS by Z. Barnea and B. Post (Barnea, 1971) gave the following values for the conventional temperature factors: $B_{Zn} = 0{\cdot}78$ (6) Å^2 and $B_S = 0{\cdot}63$ (9) Å^2. No corrections were made to the X-ray data for thermal diffuse scattering and it is estimated that these values should therefore be increased by about 0·04 Å^2. There is thus excellent agreement between the values obtained from the X-ray and neutron experiments.

All sets of neutron data consistently indicated the occurrence of effects due to anharmonic thermal vibrations of the ions as allowed by their tetrahedral site symmetry. We can determine only a single anharmonicity parameter and for convenience we have considered an effective parameter $\beta' = \beta_S + (\alpha_S^3/\alpha_{Zn}^3)\beta_{Zn}$. From the site symmetries we obtain that β_S is negative and β_{Zn} is positive. The observed values for β' are about -4×10^{-12} erg.Å^{-3} for both ZnS and ZnTe. The values obtained for β' are of the same order as the values of β_F obtained for the fluorine ions in the fluorite compounds CaF_2, SrF_2 and BaF_2.

The significance of the anharmonicity and extinction parameters was evaluated by comparing the results described above with those obtained when the values of β' and s^* respectively fixed at zero. The significance levels for these parameters were estimated from the significance tables of Hamilton (1965) using the ratio of the R index obtained with the parameter set to zero and that obtained for the original model. The R-index ratios and the resultant significance levels are listed in Table 11. Although there is some variation between the levels for various sets of data, the overall significance level for the anharmonicity parameter is about 0·05 in both cases. The extinction parameter is significant, in all cases, to the 0·01 or smaller level; for ZnS the level is considerably less than 0·005 for all sets of data. It is concluded, therefore, that both parameters can be accepted with a reasonable significance.

Table 11. *R-index ratios and significance levels for anharmonicity and extinction parameters*

(*a*) ZnS

	Anharmonicity		Extinction	
λ (Å)	*R*-index ratio	Sign. level	*R*-index ratio	Sign. level
0·873	1·04	0·200	1·95	→ 0
0·945	1·18	0·005	3·88	→ 0
1·146	1·15	0·030	2·36	→ 0

(*b*) ZnTe

	Anharmonicity		Extinction	
λ (Å)	*R*-index ratio	Sign. level	*R*-index ratio	Sign. level
0·945	1·07	0·100	1·53	0·005
1·143	1·10	0·025	1·14	0·010

A detailed study of the data indicated that there was no significant evidence of anisotropic extinction effects, even for the more severely extinguished reflections. In any case, it is unlikely that any such effects would distort the results of the analysis, particularly as far as the anharmonicity is concerned, since the contributions from anharmonicity arise only for the weaker $(h+k+l=4n\pm1)$ reflexions and increase with increasing *hkl* product. For these reflexions extinction is only a few percent, even at the longest wavelength, and for these to be affected significantly by anisotropy in the extinction would require extremely large effects to be observed for the strongest reflexions.

The present measurements provide a more reliable value of the nuclear scattering amplitude of zinc, *i.e.* $b_{Zn} = 0{\cdot}569$ (2) $\times 10^{-12}$ cm. The reliability of this value is due primarily to the precision of the recent determination of the nuclear scattering amplitude of sulphur, $b_S = 0{\cdot}2847$ (1) $\times 10^{-12}$ cm (Koester, 1971).

We are grateful to Dr Z. Barnea for correspondence concerning his unpublished X-ray measurements with Professor B. Post on ZnS.

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Parameter Refinement in the Multiple Isomorphous-Replacement Method

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The usual procedure for parameter refinement in the multiple isomorphous-replacement method leads to a heavy bias in each round of refinement towards the previously assumed values. This leads to difficulties of convergence, which can be severe when one derivative or site is overwhelmingly powerful in phase determination. The bias arises from using the parameters of a derivative in estimating phase angles, which are then used to refine these same parameters. By omitting the derivative which is to be refined from the phase determination, this bias is avoided, and even though the phases may then be very inaccurate, convergence is rapid. This method was applied to the α-chymotrypsin structure, when the conventional procedure failed to converge correctly, and led to a greatly improved electron-density map. Correct estimation of occupancy and lack-of-closure errors remains an unsolved problem.

1. Refinement methods in the isomorphous-replacement method

Refinement of the parameters of an isomorphous substituent raises difficulties in the non-centrosymmetric case, because observed differences of structure amplitude cannot be explicitly related to the calculated structure factor of the substituent until the phase angles are known. Rossmann (1960) proposed a method based on analysis of the $(\Delta|F|)^2$ difference Patterson function, using a weighting factor which implies a statistical relationship between the amplitude difference $\Delta|F|$ and the calculated scattering factor of the substituent. This method has not been used widely with three-dimensional data, though analogous methods for two-dimensional, centrosymmetric data are satisfactory (Hart, 1961; Lundberg, 1965). It remains, however, the only least-squares method available when only a single isomorphous pair is available, unless anomalous scattering data is also used (Kartha, 1965; Adams *et al.*, 1969). The alternative method of using difference or 'residual' Fourier synthesis would appear to be a laborious method of refinement, though it provides an excellent check on the correctness of the results.

In the work on myoglobin, optimum values of the x_i and z_i coordinates, occupancy Z_i and temperature factor B_i were found from the centrosymmetric ($h0l$) data by exploration of the residual function (Hart, 1961). (Throughout this paper the subscript i identifies a particular site of isomorphous substitution.) This left only the relative y_i coordinates of substituent atoms to be estimated from non-centrosymmetric data (Dickerson, Kendrew & Strandberg, 1961*a*, *b*).

Dickerson *et al.* (1961*b*) suggested that all parameters could in principle be refined simultaneously by a method similar to the one used for refining the y_i, in which rounds of least-squares refinement alternate with redetermination of the phase angles. The refinement parameter relevant to the jth derivative would be the root-mean-square lack of closure E_j (Blow &

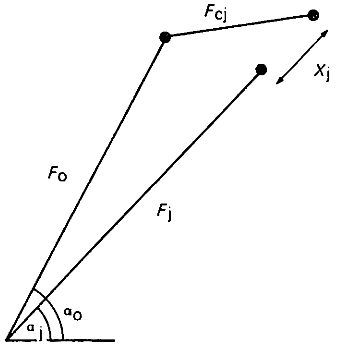

Fig. 1. The lack-of-closure vector X_j (h).

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